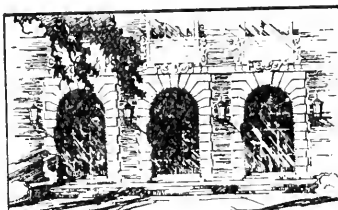


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BULLETIN No. 19

DEPARTMENT OF CERAMICS

R. T. STULL, Acting Director

## INVESTIGATION ON IRON ORE CEMENTS

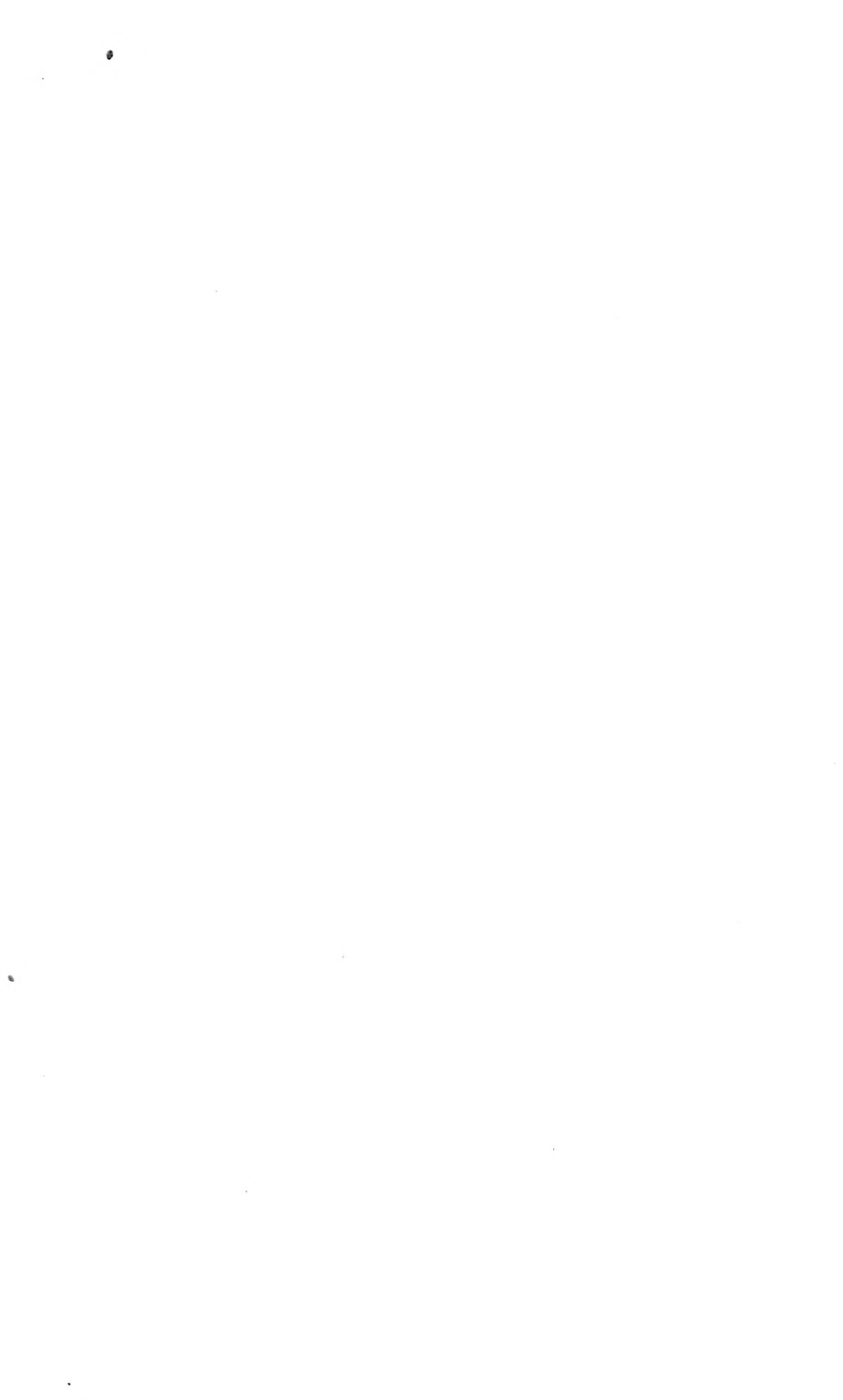
BY

ARTHUR E. WILLIAMS

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1913-1914





## IRON ORE CEMENT.\*

BY ARTHUR E. WILLIAMS.†

Iron ore cement is a product intended to be used in sea water work. This material is now manufactured in Europe under the name of Erz cement. According to Mr. William Michaelis, Jr.,‡ the process of manufacture is similar to that of Portland cement except that limestone and iron ore are used in place of limestone and clay. United States Consul Thackara§ gives a description of its manufacture as follows: Chalk, flintstone, and finely ground ferric oxide are used. The flint and iron are ground together, then mixed with the chalk and water and screened through a fine sieve. The screened product is clinkered in a rotary kiln and then ground. An average composition of iron ore cement, given by Michaelis is:

CaO.....	63.5 per cent	Al <sub>2</sub> O <sub>3</sub> .....	1.5 per cent
SiO <sub>2</sub> .....	20.5 "	MgO.....	1.5 "
Fe <sub>2</sub> O <sub>3</sub> .....	11.0 "	Alkali.....	1.0 "

The effect of sea water is undoubtedly two-fold. In the first place chemical reaction may take place between certain constituents of the cement and the salts in sea water, and, on the other hand, the mechanical action of the waves carrying large amounts of sand, freezing, thawing, and the varying pressure of the water due to tide help to injure the cement submerged in sea water. This work, however, will be confined to the chemical action of sea water, for the mechanical action is of minor importance unless the cement is weakened by chemical changes.

The reactions which take place between Portland cement and sea water are said to be of three distinct kinds. *First*, the action of MgCl<sub>2</sub> and MgSO<sub>4</sub> in sea water on the calcium hydrate formed during the hardening process of the cement, forming Mg(OH)<sub>2</sub>, CaCl<sub>2</sub>, and CaSO<sub>4</sub>. *Second*, the action of gypsum,

\* Under the direction of Mr. R. T. Stull.

† Urbana, Ill. A Thesis for the Bachelor of Science Degree in Ceramics, University of Illinois in 1910.

‡ Eng. News, Vol. 58, pp. 615-616.

§ United States Consular Reports, June, 1908.

$\text{CaSO}_4$  formed above, upon the calcium aluminates forming calcium sulpho aluminate. *Third*, the crystallization of the gypsum and calcium sulpho aluminate giving an increase in volume, thus causing the disintegration of the mortar.

That free lime is present in set Portland cements is well known. Lamine\* found 32 per cent of  $\text{CaO}$  in cement submerged in the Black Sea 15 years. Every analysis of a cement exposed to sea water shows a high percentage of  $\text{MgO}$ . Vicat† in 1840 showed this fact clearly, a cement, which was submerged in sea water for 6 months, was analyzed. A sample, taken from the surface exposed to the sea, showed 10.4 per cent  $\text{MgO}$  and 19.3 per cent  $\text{CaO}$  while the interior, which was not impaired, showed 1.87 per cent  $\text{MgO}$  and 31.33 per cent  $\text{CaO}$ .

A. Meyer‡ states that cement loses strength in sea water. The  $\text{MgSO}_4$  acting with the silicate of lime forms  $\text{Mg(OH)}_2$  and calcium sulphate. The  $\text{CaSO}_4$  reacts with the calcium aluminates ( $\text{Al}_2\text{O}_3, x \text{ CaO}$ ) of the cement, forming  $\text{Al(OH)}_3 + 3 \text{ Mg(OH)}_2 + \text{CaSO}_4 + \text{CaCl}_2$ .

Charles J. Potter§ says that  $\text{MgSO}_4$  is the most active constituent in sea water on cement. He found that  $\text{MgCl}_2$  softens cement but causes no expansion. Potter says that it is now definitely believed that magnesium salts act on the feebly combined lime and alumina compounds which on taking up water of crystallization cause bursting of the concrete. He mixed calcined red brick clay with Portland cement clinker in proportions of 6 to 10. From this mixture briquettes were made and placed, together with Portland cement briquettes, in fresh water, sea water, and sea water to which 10 per cent  $\text{MgSO}_4$  was added. Both of these cements gained strength in fresh water. In salt water, the Portland cement briquettes began to fail after 5 weeks and were disintegrated after 5 years. These cements showed blistering after one year, which was followed by expansion and bursting. The red cement improved continually but took 8 weeks to obtain the maximum strength that the Portland cement had obtained in 5 weeks. In the 10 per cent solution of  $\text{MgSO}_4$ , the Portland cement tested 500 lb. in a month and then went

\* *Le Ciment*, 1901, pp. 111-691-81.

† *Iron Ore Cement*—The P. C. Co. of Hemmoor, Hamburg, Germany.

‡ *Chemisches Central Blatt*, Vol. 73, p. 1368.

§ *Jour. Soc. Chem. Ind.*, Vol. 28.

back to zero in 1 year. The red cement began at 250 lb. and increased continually to 1015 lb. in 8 years. Mr. Potter says that the chemical combination of  $\text{CaO}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  and water is feeble and that probably accounts for the ability of magnesium in sea water to be so active.

The experiments of Dr. Michaelis\* and Le Chatelier† lead them to the conclusion that Portland cement suffers in solutions containing sulphuric acid salts, which applies to sea water. A double salt is formed composed of gypsum and calcium aluminate. This sulpho-aluminate,  $\text{Al}_2\text{O}_3, \text{CaO} + 3\text{CaSO}_4$ , is said to crystallize with 30 molecules of water, which process must be accompanied by considerable expansion. Le Chatelier says that "the main cause if not the sole cause, of the injuries which cements suffer under the action of sea water is the formation of calcium sulpho-aluminate."

Rebuffat‡ says on the contrary that sulpho-aluminates cannot exist in cements in sea water but agrees with Michaelis and Le Chatelier that calcium aluminates are the parts of cement most easily acted upon by salts in sea water.

It has been shown that calcium ferrates are formed similarly to the calcium aluminates and that alumina could be replaced by ferric oxide in Portland cement. Dr. Michaelis puts this knowledge into use with the idea of overcoming the disintegration in sea water. The result of this application is the Iron Ore cement of today.

Dr. Michaelis and the Royal Experiment Station of Charlottenburg have tested these cements in comparison with Portland cements in a very thorough manner. Mr. William Michaelis§ says in a paper read in the United States that tests of Erz cement and Portland cement were made with both neat and 3 to 1 mixtures which were placed in fresh water, sea water, and water containing five times more salt than sea water. In sea water, the Erz cement developed a much greater strength than the Portland. In the strong salt water, the strength of the Portland cement decreased rapidly while the Erz cement showed a steady gain. Briquettes were made of Iron Ore and Portland cement

\* *Ton Industrie*, 1896, p. 838.

† *Le Cement*, 1901, p. 31-32.

‡ *Ton Industrie Zeitung*, 1901, p. 272.

§ *Eng. News*, Vol. 58, pp. 645-646.

which were placed in a salt solution of five times the normal strength of sea water under pressure of 15 atmospheres for a few days. This condition destroyed the Portland cement briquettes entirely, while the Iron Ore cement increased in strength.

The Royal Experiment Station conducted similar tests to the above but much more elaborate. Two Iron Ore and three Portland cements were made into prisms, using a 3 to 1 mixture of standard sand and cement. These prisms were placed in sea water and water containing five times the percentage of salts in ordinary sea water. In addition to this, these three solutions were allowed to act upon test pieces made of cement mixed with varied amounts of gypsum. All the Portland cement mortars disintegrated in the three- and five-fold salt solutions; all the Iron Ore cement mortars remained intact and sound.

United States Consul A. W. Thackara\* investigated this cement for use on the Panama Canal. The result of his investigations was the adoption of this cement for concrete work exposed to sea water. Another point in favor of this cement is the property of slower setting. The cement is weaker than Portland for the first week, but then gradually gains strength and exceeds that of Portland.

Publications of previous experiments do not show definitely the best composition for cements giving the greatest protection against sea water. With this idea in view, the following investigations were undertaken:

The outline of procedure in these experiments is as follows: Newberry's cement formula,  $x(3\text{CaO}, \text{SiO}_2) + y(2\text{CaO}, \text{Al}_2\text{O}_3)$ , was used as a basis. Assuming, according to Newberry, that  $\text{Fe}_2\text{O}_3$  could replace  $\text{Al}_2\text{O}_3$  and form  $2\text{CaO}, \text{Fe}_2\text{O}_3$ , a triaxial diagram was plotted (Fig. 1), the three members stationed at the three corners being  $3\text{CaO}, \text{SiO}_2$ ,  $2\text{CaO}, \text{Al}_2\text{O}_3$  and  $2\text{CaO}, \text{Fe}_2\text{O}_3$ . By blending these three members, cements could be obtained containing various amounts of the calcium aluminate and the calcium ferrate.

The batch weights of these three members were calculated and about 15 kg. of each were weighed up, using practically chemically pure materials. Whiting, flint, aluminium hydrate, and red oxide of iron were the only ingredients. These batches

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\* *United States Consular and Trade Reports*, June, 1905.

were ground in a ball mill, then passed through a 200-mesh sieve; thus getting thorough mixing and a finely ground batch. The formulæ for the cements made are given in Table I.

The following cements, No. 19, 20, 21, 22, 23, 24, 25, 36, 37, 38, 39, 40, 42, 48, 49, 50, 51, 52, 53, 54, 58, 59, 60, 61, 62, and 65 on triaxial diagram were then weighed up, blunged thoroughly, and partially dried by pouring the slip into plaster molds.

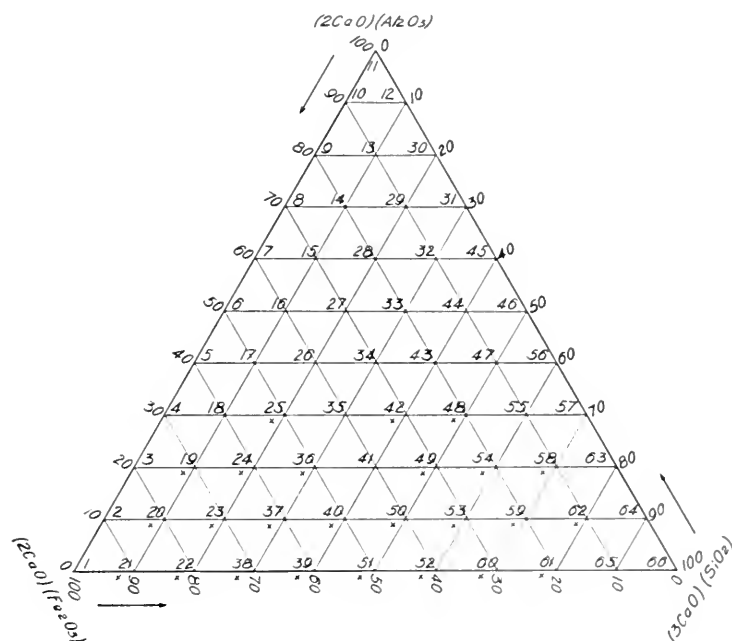


FIG. 1.—TRIAxIAL DIAGRAM.

The cements were then rolled into small balls about the size of a marble, dried, dehydrated in a down draft kiln to about  $800^{\circ}$  C. and placed in fruit jars ready for burning.

These cements were burnt in a magnesite test kiln, designed by Mr. Stull of the Ceramic Department, especially for burning experimental cements. The construction of this kiln is shown in Fig. 2. The success of this kiln is a noteworthy fact as test

kilns suitable for this purpose, heretofore, have not been very satisfactory owing to lack of control, unevenness of temperature in the clinkering chamber. Kerosene oil was used for fuel with an air pressure of about 50 lb.

The temperature at the time the clinker was drawn from the kiln was determined first by means of a Wanner pyrometer. This was given up, however, as the rapid rate of burning required a higher temperature than the true temperature of clinker formation.

TABLE I.—FORMULÆ OF CEMENTS MADE.

No.	Formulæ.	Molecular Ratio SiO <sub>2</sub> :AlO + Fe <sub>2</sub> O <sub>3</sub>
19	1(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 7(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.11
20	1(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 8(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.11
21	1(3CaO, SiO <sub>2</sub> ) + 9(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.11
22	2(3CaO, SiO <sub>2</sub> ) + 8(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.25
23	2(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 7(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.25
24	2(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 6(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.25
25	2(3CaO, SiO <sub>2</sub> ) + 3(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 5(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.25
36	3(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 5(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.43
37	3(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 6(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.43
38	3(3CaO, SiO <sub>2</sub> ) + 7(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.43
39	4(3CaO, SiO <sub>2</sub> ) + 6(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.66
40	4(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 5(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.66
42	4(3CaO, SiO <sub>2</sub> ) + 3(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 3(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	0.66
48	5(3CaO, SiO <sub>2</sub> ) + 3(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 2(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	1.00
49	5(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 3(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	1.00
50	5(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 4(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	1.00
51	5(3CaO, SiO <sub>2</sub> ) + 5(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	1.00
52	6(3CaO, SiO <sub>2</sub> ) + 4(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	1.50
53	6(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 3(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	1.50
54	6(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 2(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	1.50
58	7(5CaO, SiO <sub>2</sub> ) + 2(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 1(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	2.33
59	7(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 2(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	2.33
60	7(3CaO, SiO <sub>2</sub> ) + 3(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	2.33
61	8(3CaO, SiO <sub>2</sub> ) + 2(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	4.00
62	8(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 1(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	4.00
65	9(3CaO, SiO <sub>2</sub> ) + 1(2CaO, Fe <sub>2</sub> O <sub>3</sub> )	9.00

Almost all of these cements were fused till the surface was glassy in appearance before the cement seemed well clinkered and crystals appeared. Cements No. 54, 58, 62, and 65 appeared like a Portland clinker, except darker in color and were not fused or slag-like in appearance.

The clinker was first reduced in a jaw crusher and then ground in a disc mill; a screen test showed 24.2 per cent on 150 mesh screen; 12.3 per cent on 200 mesh screen; and the remainder, 63.5 per cent passed 200 mesh. These cements show that they are approximately of the same degree of fineness as the average Portlands. After the samples were ground, pats were made from



them in the usual manner to determine the properties of the cement.

The amount of water used for mortar was determined by the Boulouge method (Waterbury's Cement Manual, p. 44). The initial and final sets were determined with Gilmore needles.

Four pats were made of each cement with the idea of using one for the time of setting tests and placing the other three immediately in the moist closet, two of which were to be used for the boiling test after 24 hours, the third to be allowed to stand in

TABLE II.—RESULTS OF TESTS ON CEMENTS.

No.	Time of Initial Set, hours.	Time of Final Set, hours.	Water Used, per cent.	Remarks at Time of Final Set.	Conditions after 48 hours in Moist Closet.
19	1½	3	21.0	Cracked in ½ hour	Cracked
20	1	5	20.0	O. K. Strong	Warped and crackedd
21	2½	5½	21.0	No cracks	No cracks
22	12½	4	20.0	Small cracks	No cracks
23	1	..	21.0	Cracked	No cracks
24	3¼	5½	22.0	Cracked	No cracks
25	1¼	..	21.5	Cracked	No cracks. Soft
36	1¾	11	20.0	Cracked	O. K.
37	1	2½	20.0	Cracked	No cracks
38	1	5	20.0	O. K.	No cracks
39	2	8	21.0	Cracked	Cracked
40	1¼	3½	20.0	Cracked	Warped
42	1½	2¾	21.5	O. K.	No cracks
48	1¼	7	22.0	O. K.	No cracks
49	1½	3	21.0	Cracked	Cracked
50	3	..	22.0	Cracked	No cracks. Soft
51	2	10	21.0	O. K.	Soft
52	1	9	20.0	Soft	Soft
53	1¼	4	21.0	Cracked	No cracks. O. K.
54	1	4¼	23.5	Cracked	No cracks. O. K.
58	1	3¼	22.0	No cracks	Cracked
59	½	4½	21.0	O. K.	Warped
60	1½	5	21.0	Soft and crumbly	Warped and crackedd
61	1	6	22.0	Warped	O. K.
62	1½	..	22.0	Did not harden	O. K.
65	1½	..	21.0	Cracked	Warped

water for 28 days. All of these cements went to pieces in cold water or in the boiling test. The results are given in Table II.

From these cements, one only, *i. e.*, No. 62, remained sound when placed in water. This cement also stood the boiling test (½ hr.), the others going to pieces. The molecular ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  for this cement is four and since the molecular ratio for good cements is between 5.1 and 6.8 and since none of these cements lie between these limits, it was decided to construct a new group. Cement No. 62 approached these ratios nearer than any other.



A new batch was calculated after Bleiminger's formula  $(2.8\text{CaO}, \text{SiO}_2) + (2\text{CaO}, \text{Al}_2\text{O}_3)$  having different amounts of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  and also the ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  varied from just above to just below the limits. The using of chemically pure raw materials in place of slag and limestone gives less efficient mixtures of lime and  $\text{SiO}_2$ . It was, therefore, thought that sufficient lime would be obtained by the use of Bleiminger's formula. For formulæ see Table III.

TABLE III.—FORMULÆ FOR CEMENTS MADE.

No.	Formulæ				
A <sub>1</sub>	5.1(2.8CaO, SiO <sub>2</sub> ) + (2CaO, FeO <sub>3</sub> )				
A <sub>2</sub>	5.8(2.8CaO, SiO <sub>2</sub> ) + (2CaO, Fe <sub>2</sub> O <sub>3</sub> )				
A <sub>3</sub>	6.4(2.8CaO, SiO <sub>2</sub> ) + (2CaO, Fe <sub>2</sub> O <sub>3</sub> )				
A <sub>4</sub>	7.0(2.8CaO, SiO <sub>2</sub> ) + (2CaO, Fe <sub>2</sub> O <sub>3</sub> )				
B <sub>1</sub>	5.25(2.8CaO, SiO <sub>2</sub> ) + 0.175(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 825(2CaO, Fe <sub>2</sub> O <sub>3</sub> )				
B <sub>2</sub>	6.00(2.8CaO, SiO <sub>2</sub> ) + 1.75(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 825(2CaO, Fe <sub>2</sub> O <sub>3</sub> )				
B <sub>3</sub>	6.40(2.8CaO, SiO <sub>2</sub> ) + 2.00(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 800(2CaO, Fe <sub>2</sub> O <sub>3</sub> )				
B <sub>4</sub>	7.22(2.8CaO, SiO <sub>2</sub> ) + 1.75(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 825(2CaO, Fe <sub>2</sub> O <sub>3</sub> )				
C <sub>1</sub>	5.44(2.8CaO, SiO <sub>2</sub> ) + 3.60(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 640(2CaO, Fe <sub>2</sub> O <sub>3</sub> )				
C <sub>2</sub>	5.80(2.8CaO, SiO <sub>2</sub> ) + 4.00(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 630(2B <sub>1</sub> O, Fe <sub>2</sub> O <sub>3</sub> )				
C <sub>3</sub>	6.40(2.8CaO, SiO <sub>2</sub> ) + 4.00(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 600(2CaO, Fe <sub>2</sub> O <sub>3</sub> )				
C <sub>4</sub>	7.00(2.8CaO, SiO <sub>2</sub> ) + 4.00(2CaO, Al <sub>2</sub> O <sub>3</sub> ) + 600(2CaO, Fe <sub>2</sub> O <sub>3</sub> )				

PERCENTAGE COMPOSITION.					
No.	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Molecular Ratio R <sub>2</sub> O <sub>3</sub> :SiO <sub>2</sub>
A <sub>1</sub>	66.0	0.0	11.6	22.4	5.1
A <sub>2</sub>	66.7	0.0	10.4	22.9	5.8
A <sub>3</sub>	67.2	0.0	9.6	23.2	6.1
A <sub>4</sub>	67.5	0.0	8.9	23.6	7.0
B <sub>1</sub>	66.7	1.3	9.4	22.6	5.25
B <sub>2</sub>	67.1	1.1	8.4	23.1	6.00
B <sub>3</sub>	67.5	1.3	7.8	23.4	6.10
B <sub>4</sub>	68.1	0.9	7.2	23.8	7.22
C <sub>1</sub>	67.4	2.5	7.2	22.9	5.44
C <sub>2</sub>	68.0	2.7	6.0	23.3	5.80
C <sub>3</sub>	68.2	2.5	5.8	23.5	6.40
C <sub>4</sub>	68.5	2.3	5.4	23.8	7.00

These cements were prepared in the same manner except that the temperature of clinking was determined as near as possible by the method used. The kiln was allowed to cool to about 1000 deg. C. before a batch of cement was put in and temperature was then gradually raised till clinker was formed, the temperature was then read with a Wanner pyrometer.

The clinkers obtained appeared exceptionally good, being dull black in color and glistening brightly in the sun. These

clinkers were pulverized the same as has been previously described, then tested.

The results of these tests, Table IV, show that good cements can be obtained with a large amount of alumina using the same ratio of  $\text{SiO}_2$  to  $\text{R}_2\text{O}_3$  as Portland cements require. One very noticeable fact, however, is that when no  $\text{Al}_2\text{O}_3$  is present as in series A,  $A_2$ ,  $A_3$ , and  $A_4$  these cements all show expansion, thus giving evidence of free lime. Although  $A_1$  stood the boiling test, the cubes made from this cement bulged out from the mold considerably.

The question arises at this point, is it always necessary for  $\text{Al}_2\text{O}_3$  to be present or can a good cement be made without it?

TABLE IV.—RESULTS OF TEST.

No.	Temperature when Clinkered, deg. C.	Time to Clinker, hours.	Appearance of Clinker.	Initial Set, hours.	Final Set, hours.	$\text{H}_2\text{O}$ , per cent.
$A_1$	1300	$\frac{3}{4}$	.....	24	62	24.8
$A_2$	1320	$\frac{1}{2}$	All	22	56	24.0
$A_3$	1320	$1\frac{1}{2}$	clinkered	26	56	23.2
$A_4$	1330	$\frac{1}{2}$	good,	28	60	26.0
$B_1$	1390	$\frac{1}{2}$	colored black	$1\frac{3}{4}$	40	26.3
$B_2$	1320	$1\frac{1}{4}$	and	$4\frac{1}{2}$	44	24.4
$B_3$	1350	$\frac{3}{4}$	glistening	11	36	28.0
$B_4$	1400	$1\frac{1}{2}$	with	5	48	25.0
$C_1$	1320	$1\frac{1}{2}$	crystals	5	30	24.4
$C_2$	1320	$\frac{3}{4}$	in a	12	40	24.0
$C_3$	1330	$1\frac{3}{4}$	bright	12	48	28.0
$C_4$	1380	$\frac{1}{2}$	light	17	40	27.2

This ought to be possible by reducing the lime content, as  $A_1$  was the best of series A and also had the smallest amount of lime silicate.

The slowness of setting is another factor which must be considered. It will be seen by Table IV that all of the cements required a long time to harden. This must be carried on in a moist atmosphere also or the cement will dry out before it has completely hydrated and set. The above factors will perhaps limit the use of this cement to work under water which may be allowed to set a considerable time.

All the cements of series B stood a 6-hr. boiling test without showing any signs of expansion. In series C all but  $C_1$  stood the boiling test.  $C_1$  warped a little and came loose from the glass

plate although the cement has a comparatively low lime content and its formula lies between other good cements.

The attempt was next made to give these cements a comparative test with Portland cement to show their relative resistance to sea water. The method used was similar to that of Dr. Michaelis.

One-inch cubes were made of each series of cements together

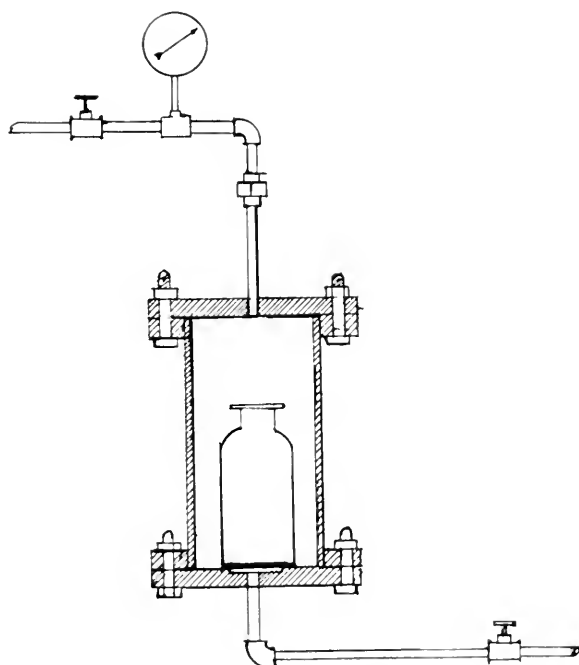


FIG. 3.—STEAM CYLINDER.

with a set of cubes of a standard commercial Portland cement, which had stood all the commercial tests. These were allowed to stand 60 hr. in the moist chamber and then placed in water, remaining in water for 27 days. The cubes made from series A together with a set of 5 Portland cement cubes were placed in a steam cylinder, Fig. 3, containing an artificial sea water solution of ten times normal strength. The quantity of salt is shown in Table V. The cements were then put under steam pressure

of 125 lb. or  $8\frac{1}{3}$  atmospheres, the temperature being between 150 and 200 deg. C. This was continued for 3 days. On opening the cylinder, the salt solution was found to be very dilute due to condensation of steam and no visible action on the cements had occurred. The salt solution and cubes were then put into a large wide-mouthed bottle, provided with a stopper and small vent hole. The bottle was then placed inside the pressure cylinder and steam admitted, allowing little or no condensation. After being sure that the bottle was not broken by the first change in temperature, the pressure was kept on for 3 days longer. Upon opening the cylinder, the cubes were found bone dry and covered with salt and the bottle cracked. This was due, no doubt, to the rapid reduction of the pressure, allowing the water

TABLE V.—ANALYSIS OF SEA WATER.\*

Salt.	Per cent of Salt.	Ten times per cent of Salt.	Total for 12 liters of Water.
NaCl.....	77.75	.....	342.10
MgCl <sub>2</sub> .....	10.87	108.7	478.28
MgSO <sub>4</sub> .....	4.73	47.3	208.12
CaSO <sub>4</sub> .....	3.60	36.0	158.40
K <sub>2</sub> SO <sub>4</sub> .....	2.46	.....	10.80
MgBr.....	0.217	.....	0.93
CaHCO <sub>3</sub> .....	0.345	.....	1.62

37.3 parts per thousand parts water.

100 parts = 2700 parts water.

12000

———— = 4.4 factor times per cent of salt = quantity per 12 liters of water.

2700

to vaporize rapidly, which was at a temperature above its boiling point.

The results of this test were contrary to what was expected as the Portland cements were untouched and all of the iron cements were cracked and swollen. This cracking and swelling is caused, no doubt, by an excess of free lime, as these cements showed an expansion in the boiling test and there was a deposit of hydrated lime in the bottom of the cylinder which seemed to have been leached out of the cubes.

No crushing strength test of Series A was made as they were all destroyed already.

Series B was then placed in the cylinder, with a set of Port-

\* *University Geological Survey of Kansas*, Vol. 7, p. 27.

land cement cubes. A vessel made of 4-in. pipe was used in place of the glass bottle to overcome cracking due to sudden change in temperature. This series was kept under pressure for 6 days, and when removed from the cylinder neither the Portland or Iron Ore cements appeared harmed except cement  $B_3$  which went to pieces. The reason for the disintegration of this cement is unexplainable except that it was not clinkered properly. The boiling test, however, showed a good cement. (Table VI.)

As the crushing strength tests of the Portlands show, there seemed to be no weakening due to being in the salt solution.

TABLE VI.—RESULTS OF BOILING TEST FOR 6 HOURS, AFTER 60 HOURS IN MOIST CHAMBER.

Number.		Appearance after Sea Water Test.
A <sub>1</sub> .....	Good.	Cracked.
A <sub>2</sub> .....	cracked plate.	"
A <sub>3</sub> .....	Came loose from plate and showed some expansion.	"
A <sub>4</sub> .....	Same as A <sub>3</sub> .	"
B <sub>1</sub> .....	Good.	Sound.
B <sub>2</sub> .....	"	"
B <sub>3</sub> .....	"	Went to pieces.
B <sub>4</sub> .....	"	Sound.
C <sub>1</sub> .....	Came loose from plate, warped.	Cracked and swollen.
C <sub>2</sub> .....	Good.	Sound.
C <sub>3</sub> .....	Good.	"
C <sub>4</sub> .....	"	"

Also the strength of the Portlands seems to average higher than the Iron Ore cements. (Table VII.)

Five cubes of each cement of Series C were then placed into the cylinder with a set of Portland cubes made at the same time. These were kept under pressure for 8 days. The results of this series were quite different as 4 of the 5 cement cubes were badly cracked and had begun to swell.  $C_2$ ,  $C_3$ , and  $C_4$  showed no signs of disintegration, but  $C_1$  was cracked and swollen badly. This cement, as the A Series, did not stand the boiling test and such an action would be expected from it under the extreme conditions in the pressure cylinder. The crushing strengths of  $C_2$ ,  $C_3$ , and  $C_4$  averaged lower than the B Series,  $C_2$  was so soft that disintegration had evidently set in.

TABLE VII.—CRUSHING STRENGTH OF CEMENTS.

No.	Cross-sectional Area, sq. in.	Crushing Strength.		Average, lb. per sq. in.
		Total lb.	Lb. per sq. in.	
<i>P</i> <sub>1</sub> = Portlands in fresh water 3 weeks.				
<i>P</i> <sub>1</sub>	1.08	7680	7100	6042
	0.975	4780	4900	
	1.06	6650	6280	
	1.045	5650	4910	
	1.105	7750	7020	
<i>P</i> <sub>2</sub> = Portland cement in fresh water 4 weeks.				
<i>P</i> <sub>2</sub>	0.97	7850	8700	7876
	0.95	6620	6970	
	0.97	7730	7960	
<i>P</i> = pressure with Series <i>B</i> of the Iron Ore Cements.				
<i>P</i>	0.97	5420	5590	6920
	1.25	1860	3890*	
	1.025	7650	7170	
	0.98	7330	7170	
	1.01	7200	7150	
Iron Ore Cement in salt solution under pressure cylinder 6 days.				
<i>B</i> <sub>1</sub>	1.035	5810	5620	5241
	1.075	6720	6250	
	1.035	5120	4915	
	1.06	4740	4160	
	1.045	5200	4860	
<i>B</i> <sub>2</sub>	1.105	7170	6500	6616
	1.02	6620	6000	
	1.055	7500	7100	
	1.115	8430	7550	
	1.125	6680	5930	
<i>B</i>	1.09	4480	4120	5014
	1.075	5180	4820	
	1.10	5000	4540	
	1.06	6610	6240	
	1.12	6000	5350	
<i>C</i> <sub>2</sub>	1.025	4200	4080	4914
	1.03	5400	4360	
	1.025	6320	6660	
	1.1	5850	5310	
	1.04	4850	4660	
<i>C</i> <sub>3</sub>	1.05	2280	2190	2110
	0.97	1580	1660	
	1.1	2640	2400	
	1.00	1820	1880	
	1.01	2500	2480	
<i>C</i> <sub>4</sub>	1.07	5220	3000	5757
	1.07	6630	6150*	
	1.06	3630	3330	
	1.07	5140	4800	
	1.04	4050	3900	
Portlands in Cylinder 7 days with Series <i>C</i> .				
<i>P</i>	0.99	3000	3030	Only unaffected Portland cement cube.
<i>P</i>	0.97	6720	6930*	

\* Signifies not calculated in average.

## CONCLUSIONS.

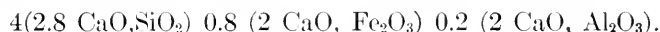
As the time for this investigation was limited, further work could not be done, and the conclusions which may be drawn from these results are limited. This much may be said, however:

1. The amount of lime or silicate of lime ought to be less when  $\text{Fe}_2\text{O}_3$  alone is used in place of  $\text{Al}_2\text{O}_3$ , as the lowest ratio of Series A 5.1 was the only one which stood the boiling test. Series B showed that the limits gave good cements throughout, neglecting  $B_3$  which must have disintegrated due to some other cause. Series C showed that the lime and silica required increased as the lower ratio 5.44 disintegrated and the higher ratios were good. To sum this up, when all iron is used the  $\text{R}_2\text{O}_3 : \text{SiO}_2$  ratio should be below 5.1; when 0.175 to 0.2 mols.  $\text{Al}_2\text{O}_3$  is used with 0.825 to 0.8 mols. of  $\text{Fe}_2\text{O}_3$  the ratios lie between 5.1 to 7.22. If 0.36 to 0.4 mols. of  $\text{Al}_2\text{O}_3$  the ratio must be 5.8 or greater. This is but a suggestion and will require further experimenting to show it definitely.

2. That cements with large amounts of  $\text{Fe}_2\text{O}_3$  will stand saline solutions better than cements containing  $\text{Al}_2\text{O}_3$  was shown in the test of Series C where the Portlands were actually disintegrated and the iron cements stood the same test.

3. The results seem to suggest that if the amount of lime was reduced lower than 2.8 CaO in Bleiminger's formula, better strength could be obtained. There was found in the bottom of the vessel, after each trial in the cylinder, a heavy muddy deposit which was principally hydrated lime and which appeared to have been leached from the cubes. This reduction of the amount of lime may not need to be as much as the results suggest if the raw materials were clay and limestone in place of pure whiting,  $\text{Al}_2(\text{OH})_6$  and flint. All of the iron cements would have stood the tests better if they had been allowed to stand in the atmosphere and age, thus giving the lime time to become calcium carbonate. The Portland cement, which these cements were tested against, was one of the best cements on the market. It tested as follows: Initial set, 3 hr.; final set  $4\frac{1}{2}$  hr.; tensile strength of neat cement after seven days, 679 lb.; after 28 days, 774 lb.; and its crushing strength is shown in the tables. This cement had also aged several months in the laboratory and was in the best of condition

to stand accelerated tests. The percent of lime given by Mr. William Michaelis is 63.5 per cent with a small amount of magnesia, MgO, 1.5 per cent. The cements made for this thesis are all above 66 per cent, this is only another evidence that these conclusions are correct and the following formula is suggested as the center of a series of cements for further experimenting:



from this vary both the amount of  $\text{SiO}_2$  and  $\text{CaO}$ .

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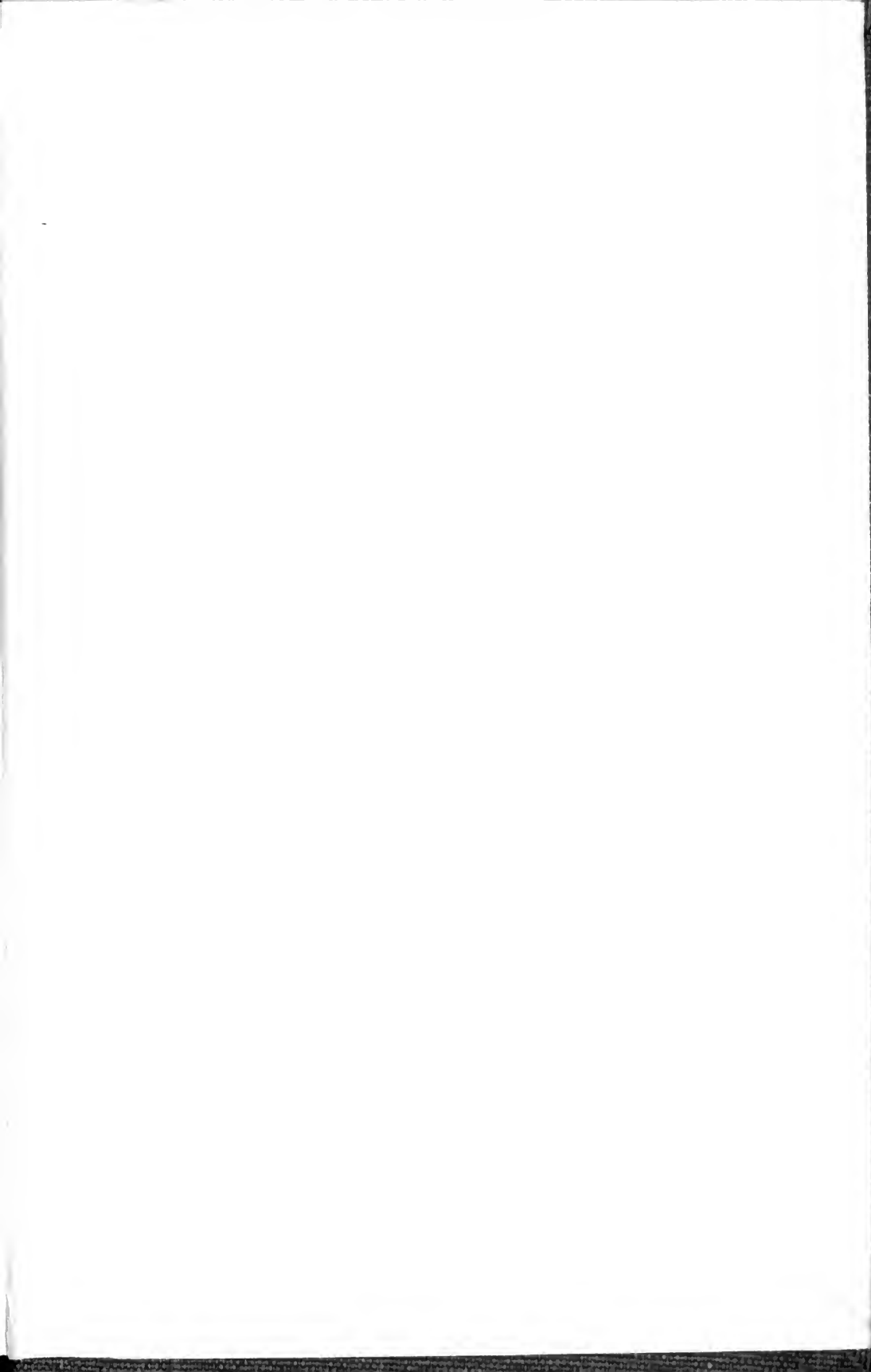












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